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VOL. XIII.] JULY, 1922. [No. 13.

On Some Isothiourea Ethers.[1]

(Contribution from the Chemical Laboratory, University of Kansas.)

BY F. B. DAINS AND W. C. THOMPSON.

ONE of the characteristic reactions of the substituted thioureas is their ability to add directly alkyl halides, with the formation of halogen halide salts of bases, in which the alkyl group is joined to sulfur.[2]

$$RNHCSNHR + R'X = RNHC(SR')NR,HX.$$

From these salts, the free thiourea ethers can be obtained by the action of alkalies. As part of an investigation now in progress, it was deemed advisable to synthesize the n-propyl and n-butyl ethers of certain thioureas and, owing to the departure of one of the authors from this laboratory, to record these preliminary results at this time.

EXPERIMENTAL.

γ-PROPYL-α, β-DIPHENYL THIOUREA. $C_6H_5NHC(SC_3H_7)NC_6H_5$.

(n-Propyl ester of phenylimino-phenyl thiocarbamic acid.)

A mixture of thiocarbanilide (15 gms.) and normal propyl iodide (10 gms.) was heated on the water bath for an hour. The light-brown viscous liquid solidified on cooling. After crystallization from alcohol the hydrogen iodide salt was obtained in the form of colorless rhombic crystals, which melted at 103°. The salt was slightly soluble in ether, cold water and cold alcohol, but readily soluble in hot water, hot alcohol and acetone. The yield was 80 per cent.

Calc. for $C_{16}H_{18}N_2S,HI$: N, 6.93. Found: 7.09, 6.79.

The free base, which was insoluble in water, was obtained by

1. The authors wish to express their thanks to the research committee of the University for a grant which was of assistance in the prosecution of this work.

2. Ber. 14, 1490 (1881); 15, 1314 (1882); 21, 962, 1857 (1888).

neutralizing an aqueous solution of the salt with sodium hydroxide. The white needles, which separated from alcohol, melted at 61.5°.

Calc. for $C_{16}H_{18}N_2S$: N, 10.39. Found: 10.10, 10.16.

γ-n-Butyl-α, β-Diphenyl Thiourea. $C_6H_5NHC(SC_4H_9)NC_6H_5$.

The mixture of normal butyl iodide and diphenyl thiourea was heated on the steam bath for an hour. The salt, which solidified on cooling, could not be purified by crystallization. It was therefore ground up and thoroughly washed with ether, in which it was insoluble. The yield of the hydroiodide, which melted at 122°, was 83 per cent.

Calc. for $C_{17}H_{20}N_2S,HI$: N, 6.78. Found: 6.66, 6.68.

An aqueous solution of the salt was treated with sodium carbonate. The free base was obtained a heavy, colorless, noncrystallizable oil, which was readily soluble in the ordinary organic solvents.

Calc. for $C_{17}H_{20}N_2S$: N, 9.85. Found: 9.92, 9.95.

γ-n-Propyl-α, β-Di-p-Tolyl Thiourea. $C_7H_7NHC(SC_3H_7)NC_7H_7$.

Di-p-tolyl thiourea and normal propyl iodide reacted readily on warming and the resulting hydrogen iodide salt was purified by washing with cold alcohol. It then melted at 165°. The yield was 88 per cent.

Calc. for $C_{18}H_{22}N_2S,HI$: N, 6.57. Found: 6.29, 6.51.

The salt was freely soluble in water and the thio ether, precipitated by the addition of alkali, crystallized from alcohol in fine, white needles which had a melting point of 99°.

Calc. for $C_{18}H_{22}N_2S$: N, 9.36. Found: 9.18, 9.35.

γ-n-Butyl-α, β-Di-p-Tolyl Thiourea. $C_7H_7NHC(SC_4H_9)NC_7H_7$.

The hydrogen iodide salt, which was obtained in a 95 per cent yield from the normal butyl iodide and the thiourea, melted at 145°.

Calc. for $C_{19}H_{24}N_2S,HI$: N, 6.36. Found: 6.35, 6.35.

The free base formed by neutralizing an alcoholic solution of the salt was a thick, colorless liquid, insoluble in water but soluble in organic solvents.

Calc. for $C_{19}H_{24}N_2S$: N, 8.97. Found: 9.12, 9.33.

γ-n-Propyl-α, β-Di-2, 4-Dimethyl-Phenyl Thiourea.
$(CH_3)_2C_6H_3NHC(SC_3H_7)NC_6H_3(CH_3)_2$.

Di-m-xylyl thiourea and normal propyl iodide reacted easily on warming, but the product, which was obtained in 87 per cent yield, proved to be the free base and not its salt. This when purified from alcohol melted at 113.5°.

Calc. for $C_{22}H_{28}N_2S$: N, 8.58. Found: 8.46, 8.46.

THIOETHERS FROM UREAS CONTAINING TWO DIFFERENT GROUPS.

γ-Methyl-α-p-Bromophenyl-β-Phenyl Thiourea.

$C_6H_5NHC(SCH_3)NC_6H_4Br$ or $C_6H_5NC(SCH_3)NHC_6H_4Br$.

The unsymmetrical nature of the mol did not prevent the addition of the alkyl iodide, since when methyl iodide and phenyl-p-bromophenyl thiourea were heated under the usual conditions a yield of 69 per cent of the hydrogen iodide salt was obtained. It melted at 152°.

Calc. for $C_{14}H_{13}N_2SBr,HI$: N, 6.24. Found: 6.04, 6.27.

The thioether was preciptated when an alcoholic solution of the salt was made alkaline with sodium carbonate and then diluted with water. When purified, the white needles melted at 79°.

Calc. for $C_{14}H_{13}N_2SBr$; N, 8.72. Found: 8.54, 8.77.

γ-n-Propyl-α-p-Bromophenyl-β-Phenyl Thiourea.

$C_6H_5NHC(SC_3H_7)NC_6H_4Br$.

Normal propyl iodide and the thiourea united to form a salt, which, however, failed to crystallize, but remained as a heavy, red oil.

Calc. for $C_{16}H_{17}N_2SBr,HI$: N, 5.88. Found: 5.46.

The thioether, which was isolated in a 70 per cent yield, melted at 84°, after purification from alcohol.

Calc. for $C_{16}H_{17}N_2SBr$; N, 8.02. Found: 8.09, 8.07.

γ-n-Butyl-α-p-Bromophenyl-β-Phenyl Thiourea.

$C_6H_5NHC(SC_4H_9)NC_6H_4Br$.

The hydrogen iodide salt from the thiourea and the normal butyl iodide separated in this case also as a thick noncrystallizable oil.

Calc. for $C_{17}H_{19}N_2SBr,HI$; N, 5.70. Found: 5.37, 5.62.

The free base obtained in the usual manner was a viscid oil, soluble in alcohol and ether.

Calc. for $C_{17}H_{19}N_2SBr$; N, 7.71. Found: 7.72, 7.52.

γ-n-Butyl-Monophenyl Thiourea. $C_6H_5NHC(SC_4H_9)NH$.

When monophenyl thiourea and normal butyl iodide were warmed on the water bath, a gummy mass was obtained. This was dissolved in hot alcohol and neutralized with sodium carbonate. On dilution with water the thiourea was precipitated as a heavy oil, which failed to crystallize.

Calc. for $C_{11}H_{16}N_2S$; N, 12.72. Found: 13.03, 13.05.

SUMMARY.

A number of new alkyl ethers of substituted thioureas have been prepared. While usually these ethers are solid crystalline compounds, the normal butyl derivatives thus far isolated are basic oils. The di-m-xylyl thiourea gave the free base and not the hydrogen iodide salt with normal propyl iodide.

LAWRENCE, KAN., July, 1922.